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Efficient and Easily Reusable Metal-Free Heterogeneous Catalyst Beads for the Conversion of CO₂ into Cyclic Carbonates in the Presence of Water as Hydrogen-Bond Donor

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Efficient and Easily Reusable Metal-Free Heterogeneous Catalyst Beads for the Conversion of CO₂ into Cyclic Carbonates in the Presence of Water as Hydrogen-Bond Donor

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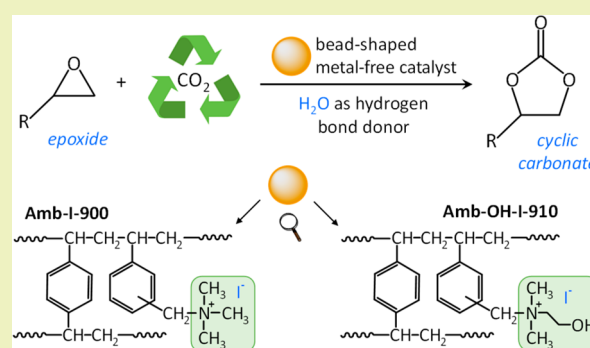
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Supporting Information

ABSTRACT: Two porous Amberlite resin beads consisting of ammonium-functionalized polystyrene cross-linked with divinylbenzene were demonstrated to be efficient, easily recyclable, and viable metal-free heterogeneous catalysts for the reaction of CO₂ with epoxides to yield cyclic carbonates. The catalysts were prepared from two affordable, commercially available resin beads, which differ in the nature of their functional groups, i.e., trimethylammonium chloride or dimethylethanolammonium chloride. These materials were converted through a straightforward ion-exchange step into their iodide counterparts (Amb-I-900 and Amb-OH-I-910). The ion-exchanged resin beads were tested as heterogeneous catalysts for the reaction of CO₂ with styrene oxide at different reaction conditions (45–150 °C, 2–60 bar of CO₂, 3–18 h). The effect of the presence of water as a hydrogen-bond donor in combination with a heterogeneous catalyst was systematically investigated here for the first time. With both catalysts, the presence of water led to higher yields of cyclic carbonate (from 12% to 58% with Amb-I-900 and from 59% to 66% with Amb-OH-I-910; ≥98% selectivity). The highest catalytic activity was observed with Amb-OH-I-910, due to the presence of –OH groups in its active site, which together with water enhanced the activity through hydrogen-bonding interactions. This catalytic system attained higher turnover numbers and turnover frequencies (TON = 505, TOF = 168 for reaction at 150 °C) and improved cyclic carbonate productivity compared to the state-of-the-art supported polymeric bead catalysts and was active in catalyzing the synthesis of styrene carbonate also at low temperature (33% yield at 45 °C and 10 bar of CO₂). Additionally, the Amb-OH-I-910 proved to be a versatile catalyst for the conversion of a variety of epoxides into their corresponding cyclic carbonates with good to excellent yields and very high selectivity (≥98%). The two polymeric bead catalysts could be easily recovered and reused without significant loss in their activity and thus represent an easily accessible, environmentally friendly, cost-effective catalytic system for the synthesis of cyclic carbonates from CO₂.

KEYWORDS: Carbon dioxide, Heterogeneous catalysis, Cyclic carbonates, Amberlite resin, Metal-free catalysts, Hydrogen-bond donors



INTRODUCTION

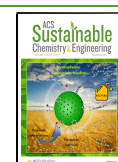
The conversion of carbon dioxide into valuable chemicals is considered a promising sustainable approach to decrease the concentration of this greenhouse gas in the atmosphere, although it should be noted that to achieve a significant impact in this sense most likely a variety of products should be targeted including both bulk and fine chemicals. A second aspect that has stimulated the investigation of the conversion of CO₂ at both an academic and an industrial level is its combination of low toxicity, availability, low cost, and renewability, which make it a very attractive C₁-feedstock.^{1,2} On the other hand, the conversion of CO₂ is rather challenging due to its high thermodynamic stability ($\Delta G^\circ = -394$ kJ/mol). To overcome this limitation, CO₂ can be reacted with molecules such as hydrogen, amines, or epoxides, which lead to a negative Gibbs free energy of reaction.^{3–6} Particularly, the cycloaddition of CO₂ to epoxides has received increasing

attention in the last decades due to the widespread applications found by the cyclic carbonate products, which can be utilized as green solvents, precursors for the production of polycarbonates, electrolytes in Li-ion batteries, and intermediates in organic synthesis.^{7–10} The use of a catalyst is crucial to achieve high rates in the reaction of CO₂ with epoxides, ideally under mild conditions.¹¹ With particular attention to metal-free catalysts, various homogeneous catalysts have been investigated for the chemical fixation of CO₂ into cyclic carbonates,

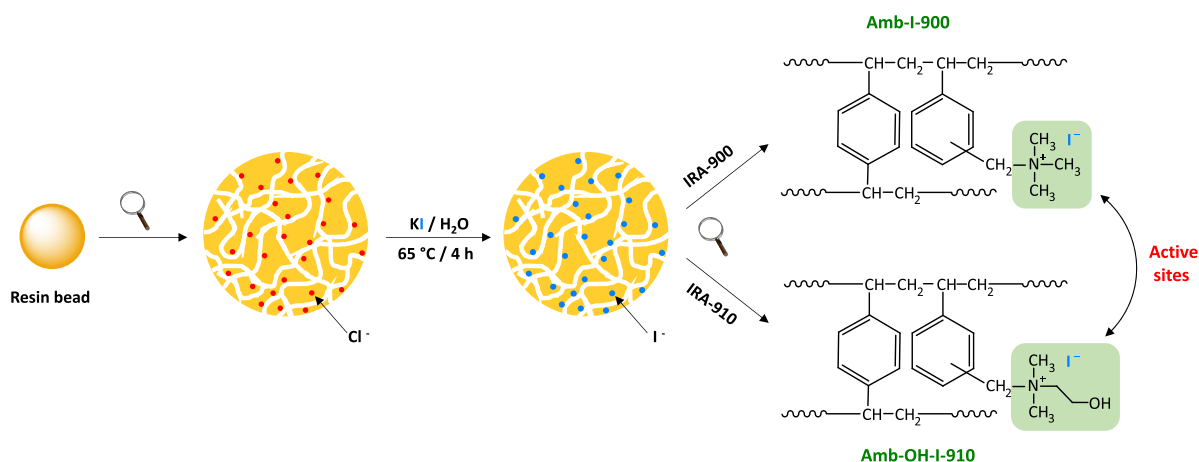
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Scheme 1. Synthesis of the Amb-I-900 and Amb-OH-I-910 Catalysts in Bead Format by Ion Exchange of the Polystyrene Divinylbenzene Resin Beads IRA-900 and IRA-910



such as quaternary ammonium salts,^{12–14} quaternary phosphonium salts,^{15,16} and ionic liquids (ILs).^{17–19} However, one of the major intrinsic drawbacks of homogeneous catalytic systems is the complicated and costly separation of the catalyst from the reaction mixture.³ To overcome this drawback, a variety of heterogeneous counterparts of the homogeneous catalysts have been developed for this reaction, in which the active species of the homogeneous organic catalysts are immobilized in a solid matrix, such as in a polymer (either by functionalization of a polymer^{20–23} or by polymerization of the active species),^{24–27} or by functionalization of high surface area silica^{28–30} or carbon-based materials (see Tables S1–S3 for an overview of the state-of-the-art metal-free heterogeneous catalysts).^{31–36} Among these catalysts, those based on functionalized cross-linked polymers typically consist of polystyrene cross-linked with divinylbenzene or of cross-linked polydivinylbenzene, grafted with diverse functional groups such as ammonium halides and imidazolium-based ionic liquids, in which the halides are the active catalytic sites acting as nucleophiles.³⁷ An efficient approach to increase the activity of these polymer-supported catalysts is to introduce hydrogen-bond donor (HBD) groups, such as hydroxyls, carboxyls, or amines, in their active sites.³⁸ These HBDs have been proposed to activate the oxygen of the epoxide through hydrogen-bond interactions in a similar way to Lewis acidic metal sites in metal complex catalysts, thus facilitating the nucleophilic attack by halides.^{38–40} An additional advantage of these polymer-supported catalysts compared to other heterogeneous catalysts for the reaction of CO₂ with epoxides is that they exist in the format of macroscopic beads (typically with a diameter of 100–800 μm), which is beneficial for their separation (if used in batch reactors) or for packing in a catalytic bed (if used in continuous reactors).⁴¹ Although these metal-free polymer-supported catalysts are effective, they still suffer from one or more limitations such as multistep and expensive synthesis procedures, the need of harsh conditions (e.g., high temperature and pressure), or high catalyst loading to achieve high carbonate yields (see Table S1 for an overview).^{37,42} Therefore, the development of metal-free heterogeneous catalysts in bead format prepared through a straightforward, low-cost route and with high activity in the reaction of CO₂ with epoxides in a wide range of temperatures

(including mild conditions), good reusability, and easy separation is a relevant research target.

Recently, we reported that water is an efficient, green, and cheap hydrogen-bond donor, which can efficiently boost the activity of organic halides (tetrabutylammonium iodide and bis(triphenylphosphine)iminium iodide) in catalyzing the reaction of CO₂ with epoxides to yield cyclic carbonates under mild conditions (even at room temperature).¹² In this work, we report for the first time the beneficial effect of water on the activity of ion-exchanged Amberlite resins as heterogeneous catalysts in the cycloaddition reaction of CO₂ with epoxides, achieving high yields of cyclic carbonates with excellent selectivity in a wide range of conditions (45–150 $^{\circ}\text{C}$, 2–60 bar of CO₂, 3–18 h). The bead format led to easy separation of these catalysts, which showed good reusability in consecutive cycles. The most promising catalytic system identified in this work combines iodide as nucleophilic species, a hydroxyl group within the active site, and water as additional hydrogen-bond donor. This catalyst achieved a remarkably high turnover number and turnover frequency (TON = 505, TOF = 168) in the conversion of styrene oxide at 150 $^{\circ}\text{C}$ and was also active at very mild conditions (45 $^{\circ}\text{C}$ and 10 bar of CO₂).

RESULTS AND DISCUSSION

Two Amberlite resin bead catalysts in iodide form were prepared by one-step ion exchange of Amberlite IRA 900 and 910 resins in Cl[−] form (Scheme 1). The parent resins consist of polystyrene cross-linked with divinylbenzene, functionalized with either trimethylammonium chloride groups (IRA 900) or dimethylethanolammonium chloride groups (IRA 910). Both resins are commercially available and exist in the form of macroscopic beads with an approximate size distribution between 500 and 800 μm (Figure S1). Their ion exchangeability, high mechanical and thermal stability, bead format, and related versatility for application in different reaction modes (batch reactors or continuous fixed-bed reactors)⁴¹ are attractive features for application as heterogeneous catalysts for the reaction of carbon dioxide with epoxides. Ion exchange of the parent resin beads with an aqueous solution of KBr or KI led to the nearly quantitative substitution of all of the chloride ions with either bromide (Amb-OH-Br-910, 97% ion-exchange efficiency) or iodide ions

(Amb-I-900, 98% ion-exchange efficiency; Amb-OH-I-910, 97% ion-exchange efficiency), as shown by elemental analysis with ion chromatography (see [Experimental Section](#) for details). The ion-exchange treatment did not affect the bead format of the resin, as shown by SEM analysis (compare [Figure 1A](#) and [1C](#) with [Figure S1](#)). This type of macroscopic resin

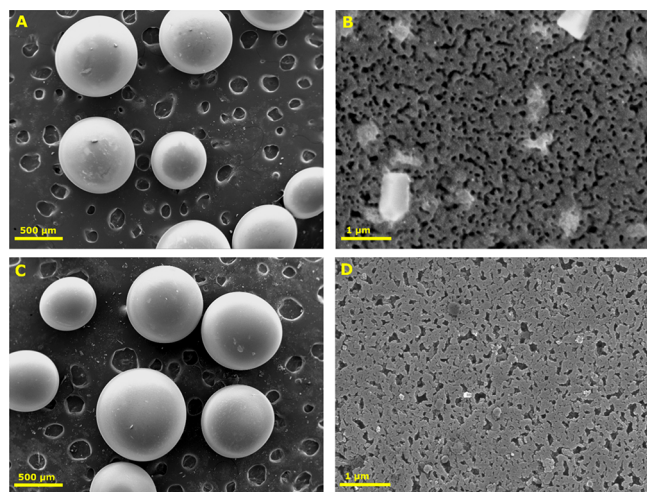


Figure 1. SEM images of Amb-I-900 ((A) whole beads; (B) surface) and Amb-OH-I-910 ((C) whole beads; (D) surface).

beads is typically characterized by an inner porous structure, which enables diffusion of molecules within the polymeric matrix.⁴³ This feature was visualized by SEM analysis ([Figure 1B](#) and [1D](#) and [Figure S1](#)), which highlighted the presence of pores with irregular, often elongated shapes ranging from the meso- to the macroscale (25–600 nm) with an average pore size of 121 nm. The CO₂ adsorption capacity of Amb-I-900 and Amb-OH-I-910 was estimated to be 22 and 12 mg_{CO2} g^{−1}, respectively, based on the adsorption isotherms measured at 298 K ([Figure 2](#)). The lower CO₂ uptake obtained with Amb-

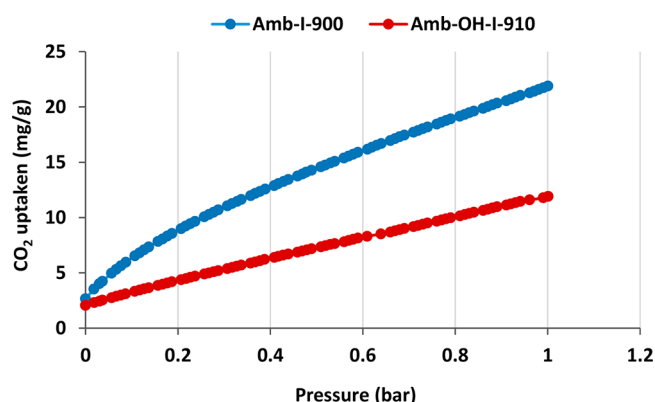


Figure 2. CO₂ adsorption isotherms (298 K) of Amb-I-900 and Amb-OH-I-910.

OH-I-910 is most likely ascribed to the bulkier ammonium group in Amb-OH-I-910 compared to Amb-I-900 ([Scheme 1](#)). FT-IR analysis was carried out for both materials. The spectra and assignment of the major peaks can be found in the Supporting Information ([Figures S11](#) and [S12](#)). The thermal stability of the ion-exchanged Amb-I-900 and Amb-OH-I-910 resin beads was investigated by thermogravimetric analysis

(TGA, [Figure 3](#)). For both types of resin beads, the TGA curve showed a small weight loss (4–5%) in the range of 50–120

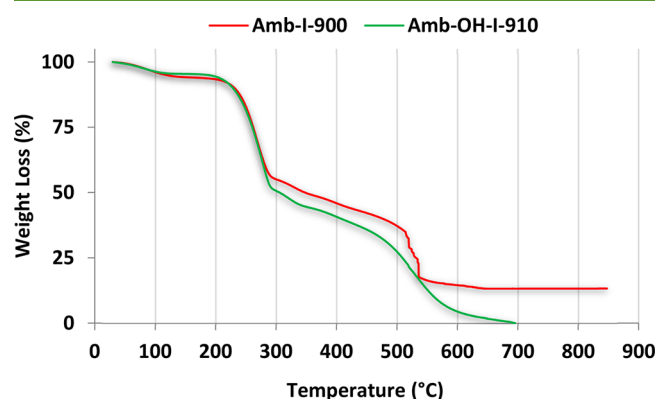


Figure 3. Thermal gravimetric analysis (TGA) of Amb-I-900 and Amb-OH-I-910 under air in the 30–900 °C temperature range.

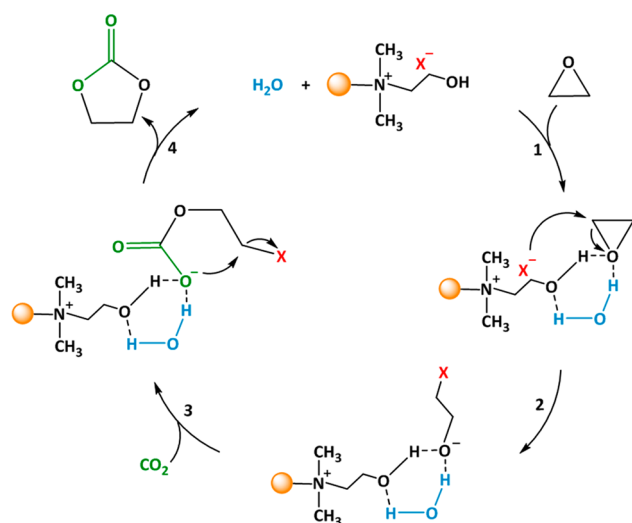
°C, which is attributed to removal of physisorbed water. No further weight loss was observed up to ca. 200 °C, after which a major weight loss in two steps was observed, due to combustion of the organic polymer structure of the materials. On the basis of this TGA analysis, the resin beads should be able to operate as catalysts also at relatively high temperature (in this work, 150 °C was chosen as the highest reaction temperature).

The first target of this work was to investigate whether the presence of an inexpensive hydrogen-bond donor (HBD) as water could promote the catalytic activity of metal-free heterogeneous catalysts for the reaction of CO₂ with epoxides to produce cyclic carbonates. For this purpose, catalytic tests were performed at 80 °C, 10 bar of CO₂, and 18 h using styrene oxide as a substrate, a resin bead as catalyst (Amb-I-900 or Amb-OH-I-910), and, optionally, 0.02 mL of H₂O (1.1 mmol) as HBD ([Table 1](#)). Under these conditions, the presence of water as HBD proved extremely beneficial in enhancing the catalytic activity of Amb-I-900, as shown by the remarkable increase in the yield of styrene carbonate from 12% in the absence of water ([Table 1](#), entry 1) to 44% in the presence of 0.02 mL of water ([Table 1](#), entry 2). This result proves the effectiveness of water as hydrogen-bond donor in boosting the activity of iodide-based heterogeneous catalysts in the fixation of CO₂ into cyclic carbonates, in line with the behavior reported recently by our group for homogeneous catalytic systems (i.e., tetrabutylammonium and bis-(triphenylphosphine)iminium iodide).^{12,44} If the active site of the catalyst already contains a hydrogen-bond donor as in the case of Amb-OH-I-910 ([Scheme 1](#)), the intrinsic activity of the catalyst is much higher compared to Amb-I-900 (compare entries 3 and 1). Also with the Amb-OH-I-910 catalyst the presence of water as additional HBD enhances the activity, though in this case the effect is much less marked, passing from 59% to 66% styrene carbonate yield (entries 3 and 4 in [Table 1](#)). This indicates a cooperative action of water and the –OH group within the active site in promoting the activity of the iodide-based catalyst ([Scheme 2](#)). The expected mechanism for the reaction of CO₂ with an epoxide to produce cyclic carbonate catalyzed by our metal-free polymer-supported catalyst with the cooperation of water as HBD involves the initial activation of the epoxide through hydrogen-bond interactions ([Scheme 2](#), step 1), which activates the epoxide

Table 1. Screening of Amb-I-900 and Amb-OH-I-910 Catalysts for the Reaction of CO₂ with Styrene Oxide into Styrene Carbonate with or without the Addition of Water as HBD^a

| entry | catalyst | water (mL) | T (°C) | yield (%) ^b | selectivity (%) ^b | TON ^c | TOF ^d | productivity (h ⁻¹) ^e |
|-------|---------------|------------|--------|------------------------|------------------------------|------------------|------------------|--|
| 1 | Amb-I-900 | 0 | 80 | 12 | ≥99 | 8 | 0.4 | 0.2 |
| 2 | Amb-I-900 | 0.02 | 80 | 44 | ≥99 | 32 | 2 | 1 |
| 3 | Amb-OH-I-910 | 0 | 80 | 59 | ≥99 | 58 | 3 | 1 |
| 4 | Amb-OH-I-910 | 0.02 | 80 | 66 | 98 | 64 | 4 | 1 |
| 5 | Amb-OH-Br-910 | 0 | 80 | 25 | ≥99 | 18 | 1 | 0.5 |
| 6 | Amb-OH-Br-910 | 0.02 | 80 | 25 | 98 | 18 | 1 | 0.5 |
| 7 | Amb-OH-Cl-910 | 0 | 80 | 13 | ≥99 | 8 | 0.4 | 0.3 |
| 8 | Amb-OH-Cl-910 | 0.02 | 80 | 6 | 90 | 4 | 0.2 | 0.1 |

^aReaction conditions: styrene oxide (20 mmol), Amb-I-900 and Amb-OH-X-910 catalysts (95 mg, with X = I, Br, Cl), mesitylene (1.5 mmol) as NMR internal standard, 10 bar of CO₂, 18 h. ^bYield and selectivity measured by ¹H NMR. ^cTurnover number, defined as mol_{cyclic carbonate}/mol_{halide}. ^dTOF = TON/h. ^eProductivity, defined as (gram_{cyclic carbonate}/gram_{catalyst})/h.

Scheme 2. Proposed Mechanism for the Cycloaddition Reaction of CO₂ to an Epoxide over Amb-OH-I-910 in the Presence of Water (X = I)^a

^aAlthough for the sake of clarity the scheme is drawn with only one water molecule interacting with the active site of Amb-OH-I-910, it should be noted that in principle several water molecules can interact with each active site, forming a more extensive H-bond network.

toward the ring opening by iodide (step 2).^{12,13,27,39,40,44,45} Then, the insertion of CO₂ occurs (step 3), creating a carbonate ion intermediate, which undergoes intramolecular ring closure leading to the cyclic carbonate product and restoring the catalytic site (step 4).

In order to study the effect of the nature of the halide anion on the catalytic activity, the performance of Amb-OH-I-910 was compared to its counterparts with bromide and chloride as anion, either with or without water as HBD. The balance between nucleophilicity and leaving ability of the halide generally plays a crucial role in defining the overall activity of the catalysts for the reaction of CO₂ with epoxides.³ When the Amb-OH-X-910 catalysts (X = Cl, Br, or I) were tested without adding water, the order of activity as a function of the halide anion was I⁻ > Br⁻ > Cl⁻ (Table 1, entries 3, 5, and 7). Since iodide is the best leaving group between the three halides, this trend indicates that under the employed conditions the ring-closure step (see Scheme 2) is the rate-determining step.^{44,46} When the same catalysts were tested in the presence of water as additional HBD, the same general order of activity was observed (Table 1, entries 4, 6, and 8).

However, if we compare the impact of using water as additional HBD with the different halides, we can observe that water was beneficial to the catalytic activity with iodide, neutral with bromide, and detrimental with chloride. A similar trend was observed when using tetrabutylammonium halides as homogeneous catalysts for the same reaction¹² and can be explained on the basis of the different magnitude of the shielding effect caused by water on each of the halides. Water molecules are protic and will thus tend to arrange around the halide anions with the partially positively charged hydrogens directed toward the halide. This causes a shielding effect that increases with the strength of the base (i.e., I⁻ < Br⁻ < Cl⁻).⁴⁷ In the case of the iodide-based catalyst, the shielding effect is the smallest and the beneficial role of water as HBD is the dominant factor, leading to the observed increase in catalytic activity (Table 1, entry 3 vs 4). On the other hand, with the chloride-based catalyst the shielding effect of water is the strongest and the consequent decrease of the nucleophilicity of the chloride overshadows the positive effect of water as HBD, leading to the observed overall decrease in activity (Table 1, entry 7 vs 8).^{12,44} In all of the tests reported in Table 1, very high selectivity toward the cyclic carbonate product was observed (≥98%), with no side products observed for the tests carried out without adding water and very small amounts of styrene glycol (<2%) as side product in the tests with 0.02 mL of water, as a consequence of hydrolysis of the epoxide ring.

The beneficial effect of water as HBD on the activity of the iodide-based catalysts was further investigated by screening different amounts of water in combination with Amb-I-900 in the synthesis of styrene carbonate at 80 °C, 10 bar of CO₂, and 18 h (Figure 4). The results demonstrated that an optimum is reached by increasing the relative amount of water to 0.05 mL, which leads to 58% styrene carbonate yield, compared to 10% when no water was added and 44% in the presence of 0.02 mL of H₂O. A further increase in the amount of water (0.08 and 0.1 mL) proved detrimental, probably because an excess of water would tend to fill the pores around the hydrophilic ammonium groups, thus hindering the access of the relatively apolar epoxide to the active sites and leading to the observed decrease in the activity of the Amb-I-900 catalyst. When a similar study of the effect of the amount of water added as HBD was carried out with Amb-OH-I-910 as the catalyst, the optimum amount of water was found to be 0.02 mL with only minor variations in activity as a function of the amount of water added in the range 0.01–0.05 mL (Figure S8). It is worth mentioning that the difference in optimum amount of water acting as HBD between Amb-I-900 and Amb-OH-I-910

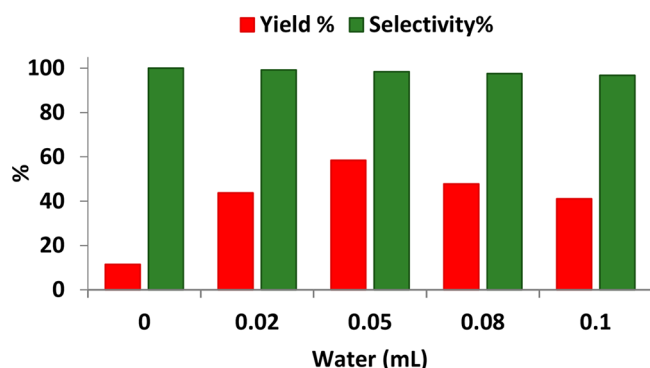


Figure 4. Effect of the amount of water employed as HBD on the catalytic activity of Amb-I-900 in the synthesis of styrene carbonate from CO₂ and styrene oxide. Reaction conditions: 20 mmol of styrene oxide, 95 mg of Amb-I-900 (0.29 mmol I), 10 bar of CO₂, 80 °C, 18 h.

is most likely related to the fact that the active site of Amb-OH-I-910 already contains a HBD (Scheme 1).

With the purpose of optimizing further the reaction conditions, the effect of CO₂ pressure was evaluated using the Amb-I-900 catalyst in the presence of the optimum amount of H₂O, i.e., 0.05 mL (Figure 5). The highest yield of styrene

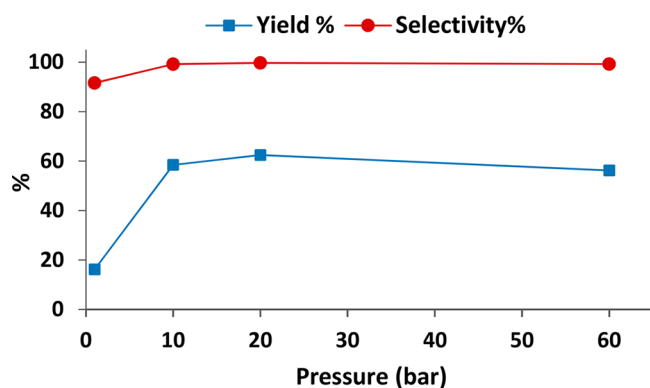


Figure 5. Effect of CO₂ pressure on the synthesis of styrene carbonate using a catalytic system consisting of Amb-I-900 and water as HBD. Reaction conditions: styrene oxide (20 mmol), Amb-I-900 (95 mg), water (0.05 mL), 80 °C, 18 h.

carbonate was achieved in the range of 10–20 bar of CO₂, always with ≥98% selectivity. At lower CO₂ pressure (2 bar), the styrene carbonate yield was dramatically lower (16%) with ≥91% selectivity. Such a drop in activity is ascribed to the

lower amount of CO₂ dissolved in the liquid phase containing styrene oxide, which under these conditions limits the reaction rate between CO₂ and epoxide. At the same time, the rate of the hydrolysis of styrene oxide into the glycol (which was the only side product) is most likely independent from the CO₂ pressure, thus accounting for the observed decrease in selectivity toward the cyclic carbonate product. Too high a pressure of CO₂ (60 bar) was also not beneficial, causing a slight decrease in the catalytic activity, most likely as a result of dilution of the reaction mixture, which decreases the probability of encounter between the epoxide molecules and the catalytic sites.^{3,48}

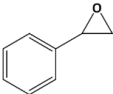
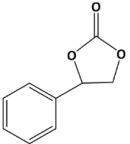

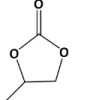
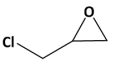
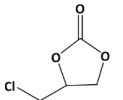
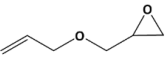
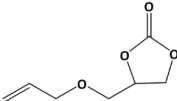
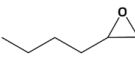
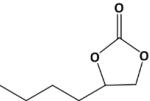

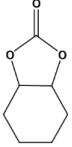
Next, we investigated the effect of the reaction temperature on the catalytic activity of the two heterogeneous catalysts Amb-OH-I-910 and Amb-I-910 (Table 2 and Figure S9). Most heterogeneous catalysts for the cycloaddition of CO₂ to epoxides operate at relatively high temperature, typically in the 100–150 °C range.^{37,49} On the other hand, there is increasing interest for catalysts that are able to convert CO₂ into cyclic carbonate under mild conditions (e.g., $T \leq 60$ °C and $p \leq 10$ bar), and several homogeneous catalysts that are able to operate efficiently under such less energy-intensive conditions have been reported recently.^{12,14,50,51} Here, we chose to explore a relatively wide range of reaction temperatures (45–150 °C), including an evaluation of the activity at high temperature but with very low catalyst loading or at low temperature but with relatively high catalyst loading. The Amb-OH-I-910 catalyst proved to be active at a very mild temperature for a metal-free heterogeneous system (45 °C), reaching 33% yield of styrene carbonate with 98% selectivity when employing a 3 mol % loading of iodide relative to the epoxide (Table 2, entry 1). The TON and TOF of our catalyst are superior to those of a previously reported metal-free heterogeneous catalyst in bead format tested at the same temperature (see Table S1). When the reaction temperature was increased from that used in the initial tests in this work (80 °C, Table 2, entry 2) to 100 °C while keeping the remaining conditions unaltered, a very high yield of styrene carbonate could be achieved (93%, Table 2, entry 3). A further increase of the reaction temperature to 120 °C enabled us to decrease the reaction time from 18 to 3 h while still reaching a high styrene carbonate yield (82%, Table 2, entry 4). Encouraged by these promising results, we decided to further increase the reaction temperature to 150 °C while substantially decreasing the catalyst loading relative to the epoxide (0.07 mol %) and shortening the reaction time (Table 2, entry 5). Remarkably, even under these challenging conditions the catalyst was able

Table 2. Effect of Temperature on the Cycloaddition of CO₂ to Styrene Oxide Using Amb-OH-I-910 Catalyst with Water as HBD^a

| entry | catalyst loading ^b | water (mL) | T (°C) | t (h) | yield (%) ^c | selectivity (%) ^c | TON ^d | TOF ^e | productivity (h ⁻¹) ^f |
|-------|-------------------------------|------------|--------|-------|------------------------|------------------------------|------------------|------------------|--|
| 1 | 3 mol % | 0.02 | 45 | 18 | 33 | 98 | 11 | 0.6 | 0.2 |
| 2 | 1 mol % | 0.02 | 80 | 18 | 66 | 98 | 64 | 4 | 1 |
| 3 | 1 mol % | 0.02 | 100 | 18 | 93 | 97 | 90 | 5.1 | 2 |
| 4 | 1 mol % | 0.02 | 120 | 3 | 82 | 96 | 164 | 55 | 9.3 |
| 5 | 0.07 mol % | 0.02 | 150 | 3 | 36 | 96 | 505 | 168 | 63 |
| 6 | 0.07 mol % | 0 | 150 | 3 | 31 | 98 | 429 | 143 | 54 |

^aReaction conditions: styrene oxide (20 mmol in entries 1–4, 60 mmol in entries 5 and 6), Amb-OH-I-910 catalyst (285 mg in entry 1; 95 mg in entries 2–4; 19 mg in entries 5 and 6), mesitylene (1.5 mmol) as NMR internal standard, 10 bar of CO₂. ^bMole percent of iodide relative to the epoxide. ^cYield and selectivity measured by ¹H NMR. ^dTurnover number, defined as mol_{cyclic carbonate}/mol_{halide}. ^eTOF = TON/h. ^fProductivity, defined as (gram_{cyclic carbonate}/gram_{catalyst})/h.

Table 3. Screening of Different Epoxides in the Reaction with CO₂ to the Corresponding Cyclic Carbonate Using Amb-OH-I-910 as a Catalyst in the Presence of Water as HBD^a

| Entry | Epoxide | Product | Yield (%) ^a | Selectivity (%) ^a | TON ^b |
|-------|--|--|------------------------|------------------------------|------------------|
| 1 |  |  | 66 | 98 | 63 |
| 2 |  |  | 95 | ≥ 99 | 81 |
| 3 |  |  | 83 | ≥ 99 | 84 |
| 4 |  |  | 65 | ≥ 99 | 64 |
| 5 |  |  | 29 | ≥ 99 | 28 |
| 6 |  |  | 37 ^c | 98 | 17 |

^aReaction conditions: epoxides (20 mmol), Amb-OH-I-910 catalyst (95 mg, 0.21 mmol I), water (0.02 mL), mesitylene (1.5 mmol) as NMR internal standard, 10 bar of CO₂, 80 °C, 18 h. ^bYield and selectivity measured by ¹H NMR. ^cTurnover number, defined as mol_{cyclic carbonate}/mol_{halide}. ^d190 mg of Amb-OH-I-910 catalyst (0.42 mmol of iodide), 30 bar of CO₂, 120 °C, 24 h.

to achieve a 36% yield of styrene carbonate, which corresponds to a very high turnover number (TON = 505), turnover frequency (TOF = 168), and productivity (63 h⁻¹). These are the highest TON, TOF, and productivity reported so far for the cycloaddition of CO₂ to styrene oxide over metal-free heterogeneous catalysts in bead format (see Table S1 for an overview). When the same test was carried out in the absence of water as HBD, the TON decreased to 429 (Table 2, entry 6), indicating that water acts as promoter of the activity of the Amb-OH-I-910 catalyst also at higher reaction temperatures.

Besides the catalysts in bead format discussed above (Table S1), several other metal-free heterogeneous catalysts in powder form have been developed and tested in the reaction of CO₂ with epoxides (Table S2). The most active among these catalysts were synthesized by including a hydrogen-bond donor group within the structure and/or by maximizing the surface area of the material.^{44,52–55} These are elegant, effective strategies to increase the catalytic activity but come at the expense of the applicability of these systems as their synthesis typically requires multiple steps (Table S2), thus increasing complexity and cost. Although the use of different reaction conditions makes a quantitative comparison difficult, it is worth noting that the performance of our optimum catalytic system (Amb-OH-I-910 with water as HBD) ranks well also among these catalysts, being surpassed only by a few of them (Table S2).^{44,54,55} On the other hand, our catalyst combines high activity with a significantly lower cost and the advantages of the bead format, making it a more viable and attractive option for large-scale application.

The influence of the reaction temperature on the cycloaddition reaction of CO₂ with styrene oxide was also examined using the Amb-I-900 catalyst (1 mol % loading relative to the epoxide) in the presence of the optimum amount of water identified in the initial tests (0.05 mL, vide supra) at 10 bar of CO₂ and 18 h (Figure S9). In line with logical expectations, the yield of styrene carbonate increased at higher reaction temperature. The selectivity toward the cyclic carbonate was 98% for reaction temperatures up to 80 °C and decreased to 96% for reaction at 100 or 120 °C with styrene glycol being the only observed side product. It is worth noting that the catalytic activity of Amb-I-900 in combination with 0.05 mL of water as HBD at 100 °C (86% styrene carbonate yield with 96% selectivity) was only slightly inferior to that of Amb-OH-I-910 in the presence of 0.02 mL of water as HBD (Table 2, entry 3).

The substrate scope of our optimum catalytic system consisting of Amb-OH-I-910 assisted by H₂O as HBD was evaluated by performing the reaction of CO₂ with a variety of epoxides at 80 °C (Table 3). Good to excellent yields were achieved, and the selectivity toward the cyclic carbonate product was nearly complete (≥99%) with all of the newly tested epoxides (Table 3, entries 2–6). The highest conversion was attained with propylene oxide (entry 2). This can be attributed to the smaller size of this compound compared to the other tested epoxides, which facilitates its approach to the active sites in Amb-OH-I-910. An additional difference compared to styrene oxide is that with propylene oxide the nucleophilic attack in the first step of the catalytic cycle (Scheme 2) takes place mostly at the less hindered carbon

atom.⁷ The catalyst showed good to excellent activity with all of the other tested terminal epoxides, with the carbonate product yield decreasing as a function of the epoxide in the order epichlorohydrin > allyl glycidyl ether > 1,2-epoxyhexane (Table 3, entries 3–5). The high conversion of epichlorohydrin is attributed to the low steric hindrance in this epoxide compared to the other two epoxides, while the difference in activity between allyl glycidyl ether and 1,2-epoxyhexane is ascribed to an electronic effect originating from the electronegativity of the oxygen atom present in the functional group of allyl glycidyl ether, which can enhance the nucleophilic attack by the halide in the first step (Scheme 2), leading to easier ring opening of this epoxide compared to 1,2-epoxyhexane.^{56,57} Our catalytic system also showed to be active with an internal epoxide such as cyclohexene oxide, which is a particularly challenging substrate due to the steric hindrance around the epoxide ring and the geometric strain in the cyclic carbonate product, which consists of two adjacent rings.⁵⁸ As a consequence, higher catalyst loading (2 mol %) and higher reaction temperature (120 °C, 24 h) were necessary to achieve an acceptably good yield of cyclohexene carbonate (37%, Table 3, entry 6). The need for a higher temperature in order to achieve good carbonate yields in the reaction of cyclohexene oxide with CO₂ is in line with literature reports of other metal-free heterogeneous catalysts, with which this reaction is typically carried out in the 110–130 °C range (Table S3).

The other catalyst employed in this study, Amb-I-900, was also investigated with different epoxides in the presence of water (0.05 mL) under the same reaction conditions described in Table 2. The results revealed that several epoxides were successfully converted into their corresponding cyclic carbonates with high yield and selectivity, with the values of the yields being very similar yet slightly lower compared to those obtained with Amb-OH-I-910 (Table S4 in the Supporting Information). This confirms that in the presence of water as HBD, Amb-I-900 is able to achieve comparable catalytic performance to Amb-OH-I-910, whereas the difference in activity between the two is marked if no water is added to the system (Table 1, compare entries 1 and 3).

The promising activity of the catalytic system consisting of Amb-OH-I-910 and water as HBD in the synthesis of propylene carbonate from CO₂ and propylene oxide prompted us to perform a test at much shorter reaction time (3 h) and at 120 °C (Table S5). Under these conditions, a high yield of propylene carbonate was achieved (88%), though the selectivity was slightly lower (96%) due to the formation of propylene glycol as side product.

To evaluate the stability of our catalytic system, reusability tests were carried out using styrene oxide as a substrate with either Amb-OH-I-910 or Amb-I-900 in the presence of water as HBD under our optimum conditions (Figure 6). The two catalysts were easily recovered by a simple procedure (see Experimental Section), which did not require filtration or centrifugation as the resin beads spontaneously and rapidly settled at the bottom of the glass reactors as soon as the stirring was stopped. In both cases, the catalyst activity slightly decreased upon recycling, though in the fourth run Amb-OH-I-910 still gave a 55% yield of styrene carbonate (compared to 65% in the first run). To investigate if the observed decrease in activity was accompanied by leaching of active species from the catalyst, a leaching test was performed in which a solution of styrene oxide (20 mmol), Amb-I-900 (95 mg), and water (0.05

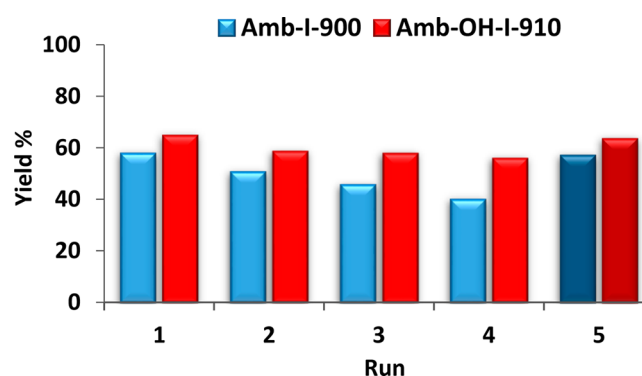


Figure 6. Reusability test of Amb-I-900 and Amb-OH-I-910 in the synthesis of styrene carbonate from CO₂ and styrene oxide. Reaction conditions: styrene oxide (20 mmol), Amb-I-900 (95 mg, 0.05 mL of water) or Amb-OH-I-910 (95 mg, 0.02 mL of water), 10 bar of CO₂, 80 °C, 18 h. Notes: Selectivity toward styrene carbonate was $\geq 98\%$ in all tests. In the fifth run, both catalysts were regenerated by washing with an aqueous solution of KI (1 M) under stirring for 4 h at 65 °C.

mL) was added into a glass vial and left under stirring at 80 °C for 18 h. Then, the solution was separated from the resin beads, placed into a reactor, and tested in the reaction with CO₂ under the same conditions used for the recycling tests (Figure 6). This test gave less than 1% yield of styrene carbonate, as determined by ¹H NMR (Figure S10). This means that the observed activity of the catalyst does not stem from active species leached out from the material. However, this does not exclude that a fraction of the active sites of the catalyst could undergo ion exchange, leading to substitution of the iodide anions with hydroxides. The latter are worse leaving groups compared to iodide anions, and would thus lead to the observed decrease in the catalyst activity in each run. This hypothesis is supported by elemental analysis of Amb-OH-I-910 after two catalytic runs, which showed the loss of 2% of the original iodide present in the catalyst. On the other hand, comparison of the FT-IR spectra (Figure S13) and SEM images (Figures 1 and S14) of the fresh Amb-OH-I-910 and of the recovered catalyst indicate that the polymeric structure of the material is not altered during the catalytic tests.

To overcome the slight decrease in activity upon recycling and restore the lost iodide anions, after the fourth run the catalysts were regenerated by washing with an aqueous solution of potassium iodide.⁵⁹ As a result, the carbonate yield with both catalysts was increased, allowing us to recover nearly the same activity as in the first run (Figure 6). It is worth noting that KI alone is virtually inactive in catalyzing the reaction under the same conditions used to test our bead catalysts (Table S6).

Prompted by this successful regeneration of our catalysts, a protocol was developed to enable recycling without drop of activity. For this purpose, after every run the Amb-I-900 catalyst was brought in contact with a 1 M aqueous solution of KI. This treatment was highly efficient in fully preserving the activity (and selectivity) of the catalyst upon reuse (Figure 7). This regeneration protocol has the potential to be upscaled as it only requires contacting the catalyst with the same aqueous solution of KI without the need of substituting it with a fresh one in each cycle.

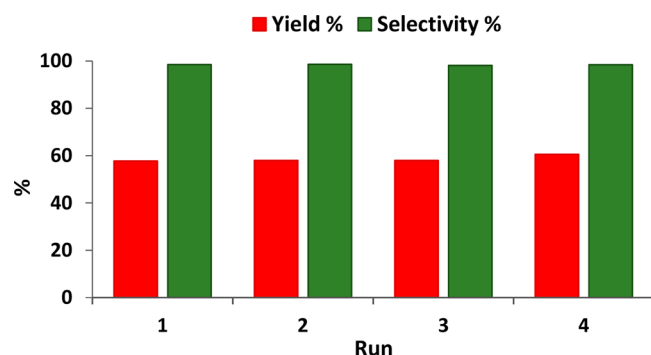


Figure 7. Reusability test of Amb-I-900 with intermediate regeneration of the catalyst by means of washing with an aqueous solution of KI (1 M) for 4 h at 65 °C (the same solution was reused during the whole procedure). The catalytic tests were carried out under the same reaction conditions described in the caption of Figure 6.

CONCLUSIONS

In this study, we proved that the most widely available, sustainable, and cheap hydrogen-bond donor, i.e. water, can efficiently boost the activity of two macroscopic Amberlite resin bead heterogeneous catalysts (Amb-I-900 and Amb-OH-I-910) in the reaction of CO₂ with a variety of epoxides toward their corresponding cyclic carbonates with excellent selectivity ($\geq 98\%$) in a wide range of conditions (45–150 °C, 2–60 bar of CO₂, 3–18 h). In the absence of water, Amb-OH-I-910 displayed significantly higher activity (59% yield) compared to Amb-I-900 (12% yield) in the synthesis of styrene carbonate from CO₂ and styrene oxide at 80 °C and 10 bar of CO₂. An enhancement in styrene carbonate yields was achieved with both catalysts if the reaction was carried out in the presence of water as hydrogen-bond donor, with the beneficial role of water being more prominent in the case of Amb-I-900 (from 12% to 58% yield). Altogether, the best catalytic performance was found with Amb-OH-I-910 owing to the presence of an –OH group in its active site, which along with water is able to enhance the catalytic activity through hydrogen-bonding interactions, allowing to attain a good yield of styrene carbonate even under mild conditions (33% at 45 °C and 10 bar of CO₂, 66% at 80 °C). This catalyst also showed excellent turnover number, turnover frequency, and productivity (TON = 505, TOF = 168, Prod. = 63 (g_{product}/g_{catalyst})/h) compared to state-of-the-art polymeric bead catalysts when the reaction was performed with low catalyst loading at higher temperature (150 °C). Besides their promising activity and selectivity in the reaction of CO₂ with a variety of epoxides, these metal-free heterogeneous catalysts display other attractive properties in the perspective of a large-scale application. Their preparation can be easily upscaled, as it involves the conversion of the two commercial resin beads in chloride form into their iodide counterparts through a straightforward one-step ion-exchange reaction. Additionally, the bead format of the catalysts allows their easy separation from the reaction mixture. Finally, recycling with full retention of catalytic activity and selectivity was achieved.

EXPERIMENTAL SECTION

Materials. 1,2-Epoxyhexane (HO, 97% purity), styrene oxide (SO, 97% purity), propylene oxide (PO, 99.5% purity), epichlorohydrin (ECP, $\geq 99\%$ purity), allyl glycidyl ether (AGE, $\geq 99\%$ purity), cyclohexane oxide (CHO, 98% purity), potassium iodide (KI, $\geq 99\%$

purity), potassium bromide (KBr, $\geq 99\%$ purity), Amberlite IRA-900 chloride form (Amb-Cl-900), Amberlite IRA-910 chloride form (Amb-OH-Cl-910), mesitylene (98% purity), and deuterated chloroform (CDCl₃, >99.6 atom %) as a solvent for ¹H NMR were purchased from Sigma-Aldrich and used without further purification. Acetone and ethanol solvents were purchased from Boom. B.V (technical grade).

Catalyst Preparation. Amb-I-900, Amb-OH-I-910, and Amb-OH-Br-910 were prepared by one-step ion-exchange reactions with potassium iodide (KI) or bromide (KBr). For Amb-I-900, 3.0 g of Amberlite IRA-900 resin beads in chloride form (3.83 mmol_{Cl}/g) was placed into a 100 mL one-neck round-bottom flask equipped with a magnetic stirrer and containing 30 mL of water. Then, a solution of KI (15 g, 90 mmol) in water (30 mL) was added into the reaction flask and left under stirring for 4 h at 65 °C. The flask was cooled in an ice bath, and then the resin beads were recovered by filtration on a sintered glass Büchner funnel. Next, the resin beads were washed with water (4 × 30 mL) and acetone (2 × 20 mL) and dried for 48 h at 70 °C to obtain an Amberlite IRA-900 in iodide form (Amb-I-900). Elemental analysis for Amb-I-900: I = 38.53 wt % (3.03 mmol_I/g), Cl = 0.22 wt % (0.062 mmol_{Cl}/g). The Amb-OH-I-910 and Amb-OH-Br-910 catalysts were prepared from the Amberlite IRA-910 resin beads in chloride form (3.39 mmol_{Cl}/g) using a similar protocol as that described above. Elemental analysis for Amb-OH-I-910: I = 27.89 wt % (2.19 mmol_I/g), Cl = 0.25 wt % (0.071 mmol_{Cl}/g). Elemental analysis for Amb-OH-Br-910: Br = 24.87 wt % (3.11 mmol_{Br}/g), Cl = 0.39 wt % (0.110 mmol_{Cl}/g).

Catalyst Characterization. Elemental analysis of the original and ion-exchanged resins was carried out at Mikroanalytisches Laboratorium KOLBE using Metrohm ion chromatography model IC 883 Plus. The surface morphology of the resin beads was investigated by scanning electron microscopy (SEM) using Philips XL30 ESEM FEG. Due to the nonconductive nature of the beads, they were coated by gold prior to the SEM measurement. Thermogravimetric analysis (TGA) of the resin beads was carried out under air from 30 to 900 °C with a 10 °C/min ramp using a thermogravimetric analyzer, TGA-4000. Fourier transform infrared (FT-IR) spectra were recorded on an IRTTracer-100 spectrometer by averaging 64 scans with a spatial resolution of 2 cm⁻¹. The CO₂ adsorption experiments were carried out on a Micrometrics ASAP 2020 device at 298 K and 1 bar.

Catalytic Tests. The catalytic tests were carried out using a high-throughput reactor manufactured by Integrated Lab Solutions (ILS), located at the University of Groningen, and described in detail in previous work from our group.^{12,58} In a typical experiment, the epoxide (20 mmol), the resin bead catalyst (95 mg, 1–1.4% loading relative to the epoxide), distilled water (0.02–0.08 mL) if employed, and mesitylene (1.5 mmol) as NMR internal standard were placed into a glass vial (46 mL volume, 30 mm external diameter) equipped with a magnetic stirring bar and closed with a screw cap containing a silicone/PTFE septum pierced with two needles for letting the CO₂ gas enter and exit the vial. Next, the glass vial was placed into the selected batch reactor, and the reactor block was closed. After this step, a software was employed to control all protocols to reach the desired reaction conditions. First, the reactor was pressurized with 10 bar of N₂, depressurized, pressurized with 10 bar of CO₂, and again depressurized to remove air. Then, the reactor block was pressurized with CO₂ (to a lower pressure compared to the target), heated up to the desired temperature, and finally further pressurized with CO₂ (if needed) to reach the chosen pressure. The reactor was kept under the selected conditions for 18 h while stirring with a speed of 600 rpm. After 18 h, the stirring was stopped and the reactor was cooled down in 20 min and depressurized to ≤ 1 bar. Finally, the lid of the reactor block was opened, and the glass vial was taken to prepare an NMR sample by adding approximately 500 mg of CDCl₃ to 50 mg of the reaction mixture. The epoxide conversion and carbonate yield and selectivity were calculated based on the ¹H NMR spectra obtained on a Varian Oxford 300 MHz or a Varian Mercury 400 MHz (see Figures S2–S7 for representative spectra) using the following formulas:

$$\text{epoxide conversion \%} = 100\% - \frac{\text{mol of unreacted epoxide}}{\text{mol of cyclic carbonate} + \text{mol of unreacted epoxide} + \text{mol of diol (if present)}} \times 100\% \quad (1)$$

$$\text{cyclic carbonate yield \%} = \frac{\text{mol of cyclic carbonate}}{\text{mol of cyclic carbonate} + \text{mol of unreacted epoxide} + \text{mol of diol (if present)}} \times 100\% \quad (2)$$

$$\text{cyclic carbonate selectivity \%} = \left(\frac{\text{cyclic carbonate yield}}{\text{epoxide conversion}} \right) \times 100\% \quad (3)$$

in which the moles of epoxide, cyclic carbonate, and diol (if present) were obtained based on integration of the respective peaks relative to integration of the peaks of the internal standard. The use of the internal standard allowed us to calculate the mass balance for all of the catalytic tests. The mass balance was in the range of 98–100% in all experiments except those employing propylene oxide as a substrate, in which case the mass balance was in the range of 85–91% because this epoxide is highly volatile even at room temperature and can thus partially evaporate during the purging of the reactor before the catalytic test and/or during the depressurization step at the end of the test. These high mass balance values imply that calculating the conversion and yield values based on the measured moles of epoxide and products at the end of the reaction (see formulas above) is a reliable approach.

Selected catalytic tests were performed in duplicate, showing a high degree of reproducibility of the obtained cyclic carbonate yields (with the variation between the two yield values being within 2%). The obtained cyclic carbonate products can be easily purified through a previously reported procedure.¹²

Note: it is worth mentioning that the stirring speed we adopted in these tests (600 rpm) is slightly lower compared to what is typically used in these reactors (900 rpm).¹² This is motivated by the observation of a partial mechanical deterioration of the Amb-OH-I-910 resin beads if the stirring speed was 900 rpm, as evidenced by the presence of a small amount of white-yellowish particles on the vial walls and bottom at the end of the catalytic tests with different epoxides. This issue was solved by changing the stirring speed from 900 to 600 rpm. A control test demonstrated that under the employed reaction conditions, the catalytic results were the same at 900 or 600 rpm, but in the latter case the resin beads remained intact.

Catalyst Recycling. After the reaction, 20 mL of ethanol was added into the glass vial that contained the reaction mixture and left under stirring for 5 min to wash and remove the product (cyclic carbonate) and other components from the resin beads catalyst. Then, the mixture was easily removed with a 150 mm capillary glass pipet. Following a similar protocol, the catalyst was washed with ethanol (2 × 20 mL) and acetone (1 × 20 mL) to further remove possible residues of impurities. After this, the glass vial containing the catalyst was placed into a vacuum oven at 70 °C for 48 h and then used in the next run.

Catalyst Regeneration Procedure. After the first washing step with 20 mL of ethanol (see previous section) and removal of the solution with a capillary glass pipet, the catalyst beads were washed with a solution prepared by dissolving KI (0.5 g) in water (3 mL). The beads were kept in suspension in this aqueous solution of KI while stirring at 65 °C for 4 h. Next, the same solution was recovered with a glass pipet and kept to be used for the regeneration step after the next run. The catalyst was washed with water (3 × 20 mL) and acetone (2 × 20 mL). Finally, the glass vial containing the catalyst was

transferred into a vacuum oven at 70 °C for 48 h and then used for the next run.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c02265>.

¹H NMR spectra of all cyclic carbonate products; additional catalytic results for Amb-I-900 and Amb-OH-I-910; tables with an overview of the performance of metal-free heterogeneous catalysts from the literature in the reaction of epoxides with CO₂; FT-IR spectra of Amb-Cl-900, Amb-OH-Cl-910, Amb-I-900, and Amb-OH-I-910; SEM images of Amb-OH-I-910 after two catalytic runs (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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